Dry regenerable CuO/γ-Al₂O₃ catalyst for simultaneous removal of SOx and NOx from flue gas

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ABSTRACT

The catalytic activity of a highly reactive and attrition resistant regenerable CuO/γ-Al₂O₃ desulfuriza-tion sorbent for NOx reduction was determined in a fluidized-bed reactor. The NO conversion over the sulfated catalyst was found to be higher than that obtained over the fresh/oxidized catalyst, with the optimum temperatures for the maximum NO removal at 350 °C for both catalysts. The decrease in NO conversion above the optimum temperature is attributed to the increase in the rate of the parallel NH₃ oxidation reaction. High levels of ammonia oxidation (i.e., >96%) was observed in absence of oxygen and NO with oxidized sorbent/catalyst, indicating the participation of the lattice oxygen ions in the CuO/γ-Al₂O₃ particles in the NH₃ oxidation reaction. The presence of steam enhances the catalytic activity of the catalysts providing a wider optimum temperature window, thus resulting in a more flexible operation for simultaneous SOx/NOx removal from flue gas.
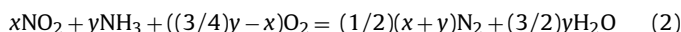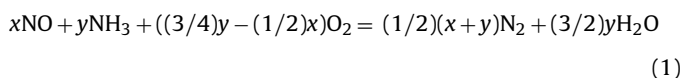
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1. Introduction

Based on EIA (US Energy Information Administration) report there will be more than 60% increase in world coal consumption by 2030 [1]. Consequently there will be a significant raise in sul-fur and nitrogen oxides emissions from coal fired power plants. To meet the environmental regulations and to minimize solid waste generation, many processes have been developed and commercial-ized to reduce emissions of SOx and NOx from coal-based power plants.

Selective catalytic reduction is regarded as one of the leading post-combustion abatement technologies for removal of nitrogen oxides. Legislations, such as the Clean Air Act (CAA) requires the NOx levels in the stack of fossil fuel-based power plants to be controlled to levels that cannot be achieved by mere combustion modifications. Selective catalytic reduction of NOx by NH₃ is a well tested technology that is capable of achieving NOx removal efficien-cies in excess of 90%. The conventional selective catalytic reduction techniques employ alumina- or titania-supported catalysts that are selective in utilizing NH₃ to preferentially reduce NO to N₂

according to the overall SCR reactions (1) and (2).

$$x\mathrm{NO} + y\mathrm{NH_3} + ((3/4)y - (1/2)x)\mathrm{O_2} = (1/2)(x+y)\mathrm{N_2} + (3/2)y\mathrm{H_2O} \tag{1}$$

$$x\mathrm{NO_2} + y\mathrm{NH_3} + ((3/4)y - x)\mathrm{O_2} = (1/2)(x+y)\mathrm{N_2} + (3/2)y\mathrm{H_2O} \tag{2}$$

The catalysts activities of various pure, supported, and/or mixed metal oxides of iron, copper, chromium, vanadia, and manganese for NOx reduction by SCR with NH₃ have been extensively inves-tigated [2]. Since SO₂ poisoning of the catalysts appears to be one of the main concerns, vanadia–titania catalysts have been consid-ered to be the most desirable oxides because of their resistance to the poisoning by SO₂ and high reactivity at temperatures around 300 °C [3–6]. Copper based catalysts are also considered to be desir-able because of their high catalytic activity in both oxide and sulfate forms. Zhu et al. [7] studied the deactivation effect of SO₂ in the NO reduction over CuO/activated carbon catalyst due to the formation of ammonium sulfate at low temperatures which can be decom-posed by heat treatment around 400 °C. In general, the results of various studies on selective catalytic reduction of NO by NH₃ over alumina supported copper-based catalysts suggest that the opti-mum NOx removal efficiency can be achieved with NH₃/NOx ratio in the range of 1.0–1.2 [8–10].

Monolithic honeycomb catalysts have been recognized as a very advantageous structure because of their good mechanical strength,

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high geometric surface area, low flow resistance and pressure drop. However NOx removal efficiency gradually decreases due to plugging by fly ash in the straight channels structure of monolith honeycomb catalyst [11]. Fluidized-bed configuration offers a number of advantages over the honeycomb structure which includes better gas solid contacting and smaller reactor size. However, one of the major issues concerning fluidized bed applications is excessive sorbent attrition, requiring mechanically strong catalysts to minimize attrition losses. Irfan et al. [12] evaluated NO removal over CuO/γ-Al_2O_3 catalyst in a bubbling fluidized bed and determined the effect of fluidizing gas velocity, NH_3 to NO molar ratio, and the static bed height on the reduction of NO at various temperatures. However the attrition properties of the sorbents were not addressed.

Although NOx removal by SCR has reached commercialization and is widely used, because of the persistent problems associated with sorbent poisoning by SO_2 and ammonium sulfate formation, it is desirable to remove SO_2 from flue gas before the SCR stage. In this regard, development of high temperature processes involving regenerable sorbents upstream of the SCR has received much attention. These processes offer a number of advantages over the established once-through low temperature lime-based processes which include, among other, elimination of significant reduction in waste generation and higher overall process efficiency. However, one of the major issues concerning regenerable sorbents is the long term durability of the sorbents, which is more pronounced if fluidized bed is utilized for desulfurization. Therefore, highly reactive and mechanically strong (i.e., attrition resistant) sorbents are required to minimize fresh sorbent make-up rate [13,14].

Various metal oxide sorbents and experimental techniques for preparation of regenerable sorbents for removal of SO_2 from flue gas have been proposed and developed. Calcium oxide impregnated with copper-alumina has been studied by Pandey et al. [15]. Bienstock et al. [16] studied sodium oxide on alumina support in the temperature range of 300–350 °C and thermal regeneration of the sulfate in the range of 650–700 °C. Demirbas [17] studied SO_2 sorption capacity of Zeolite which is extensively used as commercial adsorbent.

It has been shown that ceramic sorbents synthesized by the sol–gel method generally possess high surface area and mechanical strength [10,13,14,18,19]. Zhao et al. [20] reported higher reactivities for both the fresh and the sulfated sol–gel derived compared to the wet-impregnated CuO/γ-Al_2O catalysts in SCR of NO by NH_3. The lower reactivity of the impregnation derived sorbents may be attributed to the high thermal treatment temperature necessary for increasing mechanical strength, which diversely affects the reactivity of the sorbents by lowering their surface area and porosity [18,21]. Furthermore, these studies have shown that copper based sorbents prepared by a sol–gel method are very effective in removing SO_2 from flue gas. For example, Gavaskar and Abbasian [13] used a simplified sol–gel technique to develop a number of highly reactive and attrition resistant copper oxide sorbents which are capable of removing about 96% of SO_2 from flue gas in fluidized bed reactor.

With the recent interest in the development of multi pollutant sorbents, utilization of dry regenerable sorbents for SO_2 removal can become significantly more attractive if the sorbents can simultaneously remove SO_2 and NOx, eliminating the need for employing a separate SCR unit. However, combining the sulfur removal and NOx reduction within a single reactor will require development of sorbent/catalyst that are durable with respect to both processes. The demand for sorbent/catalyst durability is even more stringent of the sorbent/catalyst is used in a fluidized bed environment.

Different metal oxide sorbents/catalysts have been studied as potential candidates for combined SOx/NOx removal. Ma et al. [22] studied activated coke impregnated with Vanadium oxide (V_2O_5)

for simultaneous removal of SOx and NOx in a two stages process, where SO_2 removal was carried out in the first reactor and NOx reduction with NH_3 (SCR) in the second reactor. Among many metal oxide based sorbent studied for the simultaneous SOx/NOx removal, copper-oxide based sorbents appears to be one of the most promising options because of its high reactivity for SOx removal, high catalytic activity for NOx reduction, and its essentially isothermal regeneration with a reducing gas.

In regenerative copper-oxide based processes for simultaneous SOx and NOx removal, flue gas containing of N_2, CO_2, H_2O, O_2, SO_2, and NOx is passed through the desulfurization (or sulfation) reactor containing the sorbent. SO_2 reacts with the reactive component of the supported sorbent (i.e., CuO and O_2) to form copper sulfate ($CuSO_4$). The desulfurization reaction is carried out at a temperature in the vicinity of 400 °C, and may be represented by the following reaction:

$$CuO + SO_2 + (1/2)O_2 = CuSO_4 \qquad (3)$$
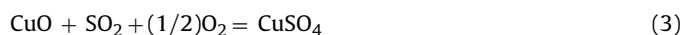
The sulfated sorbent is regenerated by a reducing gas, such as methane (CH_4), decomposing the sulfate to elemental copper (Cu) and a saleable concentrated SO_2 by-product stream. The regeneration reaction may be described by the following reaction:

$$CuSO_4 + (1/2)CH_4 = Cu + SO_2 + (1/2)CO_2 + H_2O \qquad (4)$$
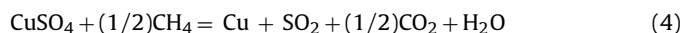
Following sulfate decomposition in the regeneration vessel, the sorbent is sent back to the desulfurization unit for re-use. Upon exposure to flue gases, elemental copper is readily oxidized to CuO, thereby fully restoring the sorbent to its original condition [9,10,13,14,18–20,23].

The reaction chemistry for NOx reduction with ammonia is complex, especially in the presence of SO_2, O_2, HCl, N_2, CO_2 and H_2O. Sirdeshpande et al. [24] provided a detailed list of the reactions that can be expected in the SCR system. The reactions are broadly classified as main reactions responsible for the reduction of NO and side reactions consuming ammonia to produce unwanted side products. It has been reported that the flue gas components such as HCl and CO_2 can indeed react with the NH_3 thus reducing its availability for the desired SCR reaction.

The main SCR reaction in the presence of oxygen is:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (5)$$
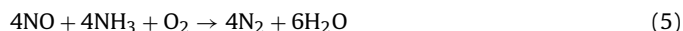
While, in the absence of oxygen, nitrogen oxides are reduced by ammonia according to

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (6)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad (7)$$

In addition to these reactions, direct oxidation of ammonia may occur producing NO, N_2O or N_2

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (8)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (9)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (10)$$

Bosch and Janssen [25] have reported that the reaction (5) is the predominant reaction under flue gas conditions, that is, dilute mixtures of NO and NH_3 with O_2 in large excess. It has also been reported that oxidation of NH_3 to N_2 also occurs in the absence of gaseous oxygen [26]. The above oxidation is supposed to take place via the lattice oxygen in the CuO/γ-Al_2O_3 catalyst as follows:

$$4NH_3 + 3CuO(s) \rightarrow N_2 + 3H_2O + Cu(s) \qquad (11)$$
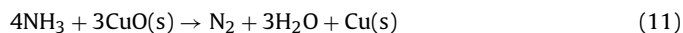
Utilization of copper oxide based sorbents/catalysts for simultaneous SOx/NOx removal has been studied by many investigators.
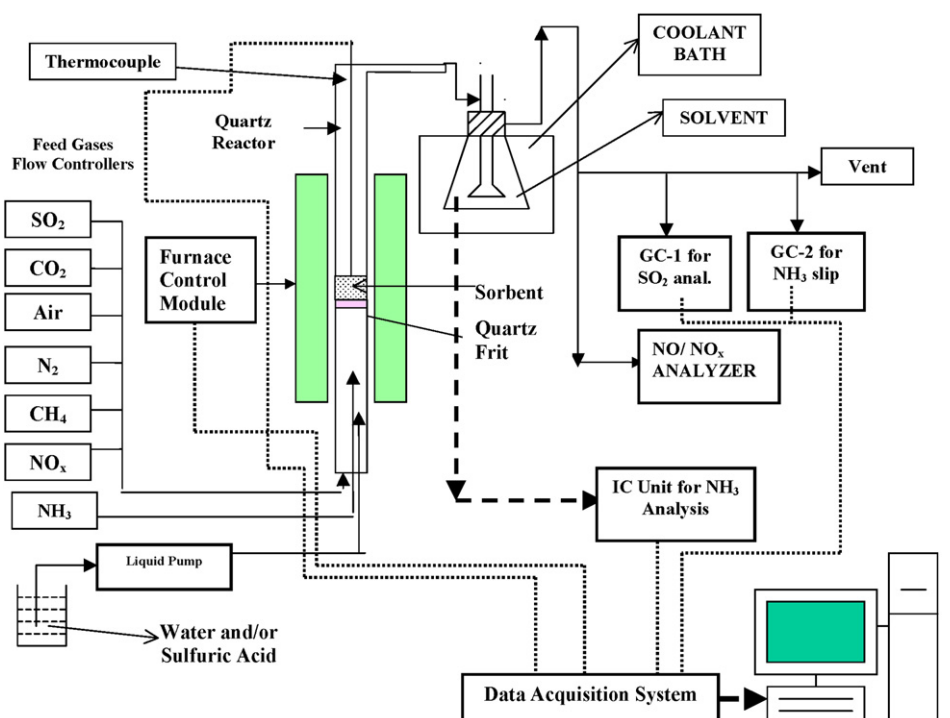
Fig. 1. Schematic diagram of the experimental setup.

[7,8,27,28]. However most of these studies were conducted in honeycomb or fixed bed reactors and the sorbent attrition were not addressed.

This paper addresses the catalytic activity of a CuO/γ-Al$_2$O$_3$ sorbent/catalyst prepared by a modified sol–gel technique, which has been shown to be capable of removing about 96% of SO$_2$ from flue gas in fluidized bed reactor. The attrition index of this sorbent, determined by ASTM-5757 technique [29], was about 8 times lower than that of a commercially available alumina-supported wet-impregnated copper oxide sorbent and 4 times lower than FCC catalyst, making the sorbent suitable for fluidized bed application [13,14]. The experimental results on the catalytic activity of the sorbent/catalyst are presented and the effects of operating variable on the extent of NOx removal as well as NH$_3$ slip with both regenerated and sulfated sorbents are discussed below.

2. Experimental

2.1. Catalyst preparation

The sorbent/catalyst used in this study was a CuO/γ-Al$_2$O$_3$ material which was prepared by modified sol–gel technique. The detailed description of the preparation method has been reported in the earlier publication [13]. The attrition resistant sorbent/catalyst (i.e., Cu-2) has been shown to remove over 96% SO$_2$ with the sulfur loading of 2.4%, while maintaining over 80% of its initial sulfur capacity over 25 adsorption/regeneration cycles [13]. The physical and chemical properties of the sorbent/catalyst are presented in Table 1.

2.2. Experimental procedure

The catalytic activity of the Cu-2 sorbent/catalyst for NOx reduction was determined in a fluidized-bed reactor. The schematic diagram of the fluidized-bed unit is presented in Fig. 1. The system consisted of a batch fluid-bed reactor, a feed gas flow control system, and a computer data acquisition system as well as a gas

chromatograph, an ion chromatograph, and a NOx analyzer for analyzing the exit gas concentrations. The fluid-bed reactor was made of quartz tube of approximately 2.5 cm i.d. The tube consisted of a quartz frit, which acted as the distributor for the upward flowing gas. The flow rates of the incoming gases were controlled using mass-flow controllers. The temperature was measured using a thermocouple in the middle of the bed, and the data was recorded using a data acquisition system. In all the experiments the volume of the sorbent bed was kept constant at 10 cm^3 and most of the runs were carried out with the gas space velocity of 4000 hr^{-1}.

In a typical experiment a known quantity of the sorbent/catalyst is loaded into the reactor and the reactor is brought to the predetermined temperature. At this point the feed is switched to simulated flue gas mixture containing the desired level of NH$_3$ and NO without SO$_2$. The baseline operating conditions as well as the ranges of the operating conditions are presented in Table 2. A NO$_X$ analyzer (Eco Physics, Model CLD 82S) was used to measure the NOx concentrations of the reactor feed and effluent. To determine the NH$_3$ content of the reactor exit gas, the gas was bubbled into a known volume of de-ionized water sample and the solution was analyzed by an ion chromatograph (IC) in 15 min intervals. The NOx reduction tests were conducted with either the fresh (oxidized) or reacted (sulfated) catalyst. When sulfated catalysts was used, the sorbent was first sulfated using a simulated flue gas containing 2500 ppmv SO$_2$ until the concentration of SO$_2$ in the reactor exit reacted 100 ppmv, which generally resulted in sulfur loading in the range of 2–2.5%. During the pre-sulfation period, a gas chromatograph (Shimadzu,

Table 1
Physical and chemical properties of the sorbent/catalyst.

Copper content (wt%)	13.2
Aluminum content (wt%)	41.1
BET surface area (m^2/g)	150
Pore volume (cm^3/g)	0.217
Avg. pore diameter (Å)	45
Bulk density (g/cm^3)	0.92
Attrition index (%)	0.9

Table 2
Baseline and ranges of operating conditions.

	Range	Baseline
Temperature (°C)	250–500	450
Space velocity (hr^{-1})	4000	4000
Gas composition		
H$_2$O (vol%)	0–10	0
O$_2$ (vol%)	0–3.7	3.7
SO$_2$ (ppmv)	0	0
NO (ppmv)	0–500	500
NH$_3$ (ppmv)	0–1000	500
N$_2$ (vol%)	Balance	Balance

USA; Model GC-17A) and an ion chromatograph (Dionex, USA; Model IC-25) were used for the determination of the SO$_2$ content of the reactor feed and effluent. The NOx reduction tests, the NOx content of the reactor reached quickly reached the steady-state level and the test continued until 1 hour of steady-state operation was achieved. The NOx concentrations in the reactor exit during the steady-state period were stable with very small fluctuations.

3. Results and discussion

3.1. Effect of temperature

In the envisioned copper oxide process, both SO$_2$ removal and NOx reduction are simultaneously accomplished in a single fluidized bed reactor. Depending on the regeneration scheme, the sorbent/catalyst in the absorber will consist of particles with different distributions in terms of their extent of sulfation. Therefore, to evaluate the catalyst for NOx removal, it is imperative to determine the activity of the catalyst in both the oxidized and sulfated state.

The effect of reaction temperature on NOx reduction with both oxidized and sulfated CuO/γ-Al$_2$O$_3$ catalysts at NH$_3$/NO ratio of 1 (500 ppmv) is shown in Fig. 2. The results indicate that in general the activity of sulfated catalyst is higher than the oxidized catalyst. Similar results have been reported by other investigators [20,27,30]. The higher catalytic activity of the sulfated catalyst has been attributed to the increases in the superacidity and the Brønsted acidity that are caused by the surface ion of SO$_4^{2-}$ on the catalyst [31]. The results also indicate that the highest conversion is generally achieved in a temperature range of 300–400 °C, which is consistent with the trend reported by other investigators [24,29,32]. The decrease of NO conversion at higher temperature may be attributed to the increase in parallel NH$_3$ oxidation reaction, as given by reaction (10), which causes a decrease in the surface ammonia for the SCR reaction with NO (reaction (5)) [30].
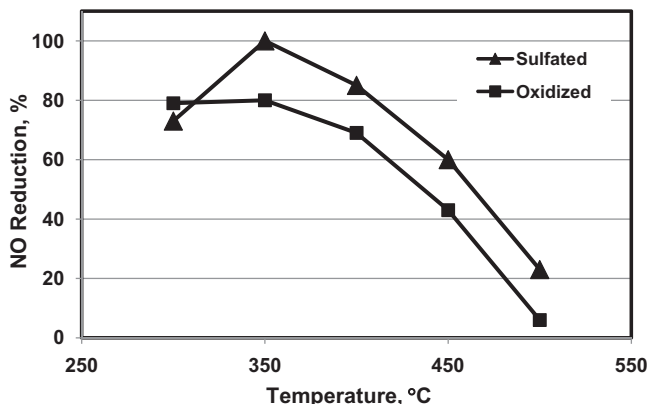

Fig. 3. Effect of temperature on NH$_3$ oxidation.
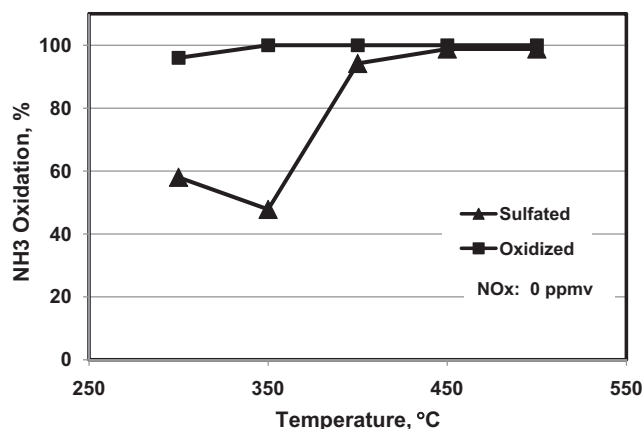
3.2. NH$_3$ oxidation

The effect of the reaction temperature on NH$_3$ oxidation on the sulfated and oxidized catalyst in the absence of NOx is presented in Fig. 3, indicating that the NH$_3$ oxidation over the oxidized catalyst is consistently higher than that over sulfated catalysts. Similar results have also been obtained by other investigators [20,27,30]. It has been reported that in the case of sulfated catalysts, NH$_3$ may be adsorbed on the sulfated surface [Al$_2$(SO$_4$)$_3$ and CuSO$_4$] of the catalyst, leading to the formation of ammonium sulfate, which decomposes at temperatures above 350 °C, and thereafter oxidized [30,31]. It can be seen from Fig. 2 that NO conversion over the sulfated catalyst starts to decrease above 350 °C.

3.3. Effect of oxygen on NO reduction

Given that oxygen plays an important role in the NO reduction and NH$_3$ oxidation, a series of experiments was conducted with oxidized catalyst at different temperatures to investigate the effect of oxygen on NO reduction and the results are presented in Fig. 4. The results indicate that the extent of NOx reduction in the presence or absence of the gaseous oxygen is essentially the same except at 300 °C. This suggests that NO reduction in the absence of oxygen either takes place via reaction (6) which will lead to the conclusion that the rate of NO reduction in reactions (5) and (6) are very similar, or that the reduction of NO in both cases takes place via reaction (5), and that the required oxygen for reaction (5) in the absence of gaseous oxygen is provided by the participation of the lattice oxygen ions in the CuO/γ-Al$_2$O$_3$ crystal [30]. The higher conversion (100%) at 300 °C in the test without oxygen (compared to 80% with
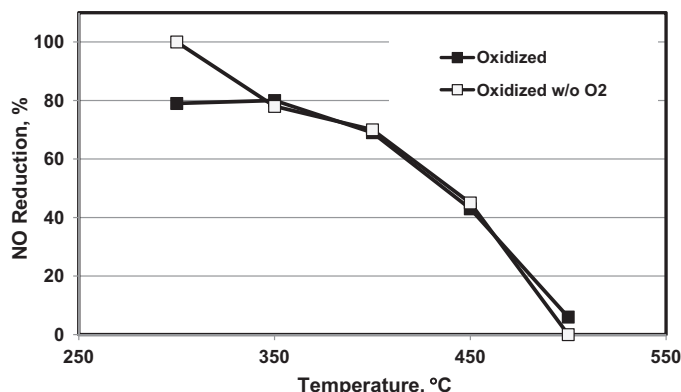

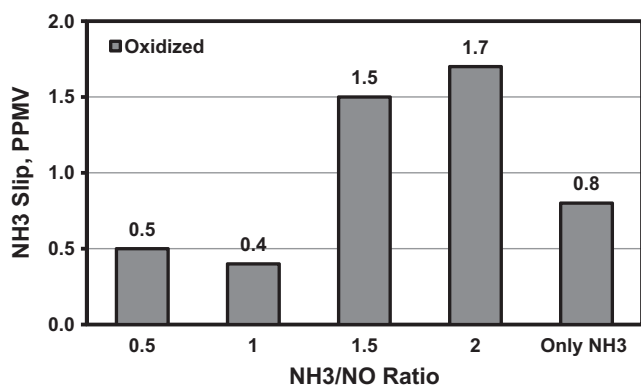**Fig. 2.** Effect of temperature on NO conversion.

Fig. 4. Effect of oxygen on NO conversion.

Fig. 5. Oxidation of NH_3 in absence of oxygen at 450 °C.

Fig. 7. Effect of steam on NO conversion (sulfated catalyst).

oxygen) may suggest that the rate of SCR reactions 300 °C are lower than those of ammonia oxidation with gaseous oxygen (reactions (7)–(9)), lowering the availability of ammonia for the SCR reactions.

Oxygen is also expected to play an important role in the NH_3 oxidation reaction. The unreacted NH_3 (slip) at 450 °C over the oxidized catalyst in the absence of oxygen as a function of $[NH_3]/[NO]$ ratio is given in Fig. 5. Comparison of the results in Figs. 4 and 5 confirm that over 50% of ammonia is in fact oxidized by another oxygen carrier other than NO at 450 °C. It can thus be concluded that the oxygen required for the above oxidation reaction is provided by the lattice oxygen ions in the CuO crystal. In another experiment which was conducted with the catalyst using a NH_3/N_2 mixture, the exit NH_3 concentration was 0.8 ppmv, which further support the above conclusion.

The effect of oxygen on NO reduction over the sulfated catalyst is shown in Fig. 6. The results follow a similar trend as the one seen in presence of oxygen, with the optimum temperature for the SCR reaction being 350 °C. It is also seen that the NO reduction in the absence of oxygen is consistently lower than that observed in the presence of oxygen, which may be attributed to the differences in the rate of reactions involving lattice oxygen ion in the sulfated catalyst. The decrease in the NO reduction above 350 °C in the absence of oxygen can be attributed to ammonia oxidation by the lattice oxygen ion in the sulfated catalyst [30].

3.4. Effect of steam

Fig. 7 shows the effect of steam (10%) on the NO removal at different temperatures over the sulfated catalyst, indicating that the presence of steam enhances the activity of the sulfated catalyst. Similar results were also obtained with oxidized catalyst (see Fig. 8).
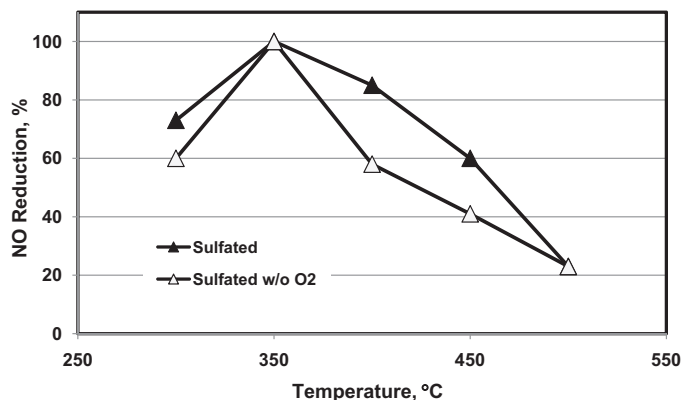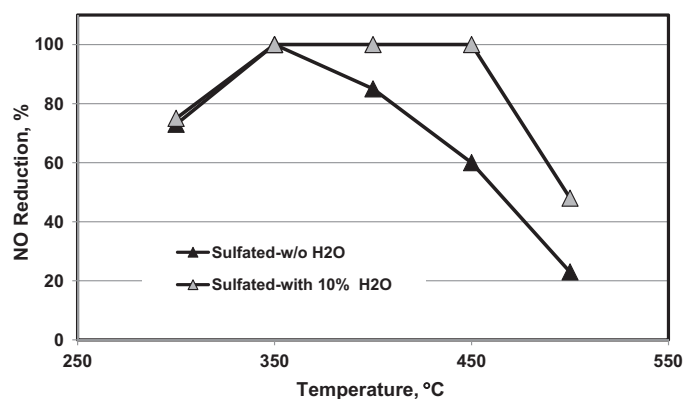
The results suggest that 100% NO reduction is possible when steam is present in the flue gas in the temperature range of 350–450 °C.

The beneficial effect of steam on the extent of NO reduction can be attributed to either a decrease in the oxidation rate of NH_3 in presence of steam, or enhancement of the catalytic activity of the catalyst because of catalyst interaction with the steam resulting in a more favorable morphology. It has been reported in the literature [33] that the presence of steam can lead to crystallization of the copper sulfate, which results in opening the pores of the sulfate product, thus providing more surface area for the SCR reaction to occur. This may result in more NH_3 being adsorbed on the sulfate surface thus leading to increased availability of the surface NH_3 and enhancing the efficiency of the catalyst. In the case of oxidized catalyst, the presence of steam can lead to the transient formation of ammonia, ammonium hydroxide or carbonate, which upon decomposition can result in a more favorable morphology.

The higher levels of NOx reduction and the wider range of optimum temperature operation observed in the presence of steam is fortuitous because the optimum operating temperature for desulfurization with the same sorbent/catalyst has already been shown to be around 400–450 °C [13], indicating that essentially complete reduction of NOx can be achieved with this sorbent/catalyst in a regenerative process for simultaneous SOx/NOx removal [34].

3.5. Effects of $[NH_3]/[NO]$ ratio

Given that the optimum NH_3/NOx is an important variable in the SCR process, which can affect the extent of NOx reduction, unreacted NH_3 (slip), and the operating cost, a series of tests was conducted at different NH_3/NO ratio at 450 °C over the sulfated catalyst. The results of these tests are presented in Fig. 9, indicating that 100% NO conversion can be achieved at NH_3/NO ratio above 1:1. A
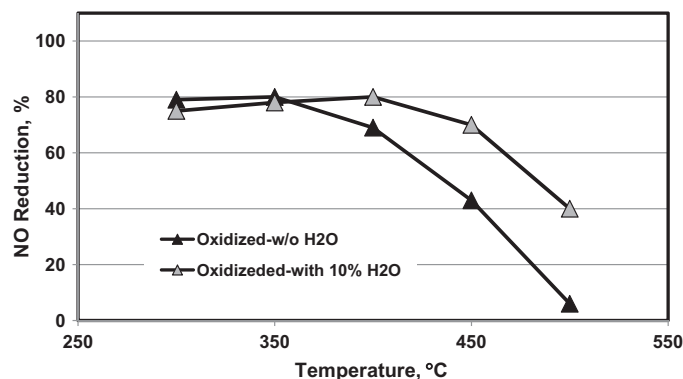

Fig. 6. Effect of oxygen on NO conversion (sulfated catalyst).

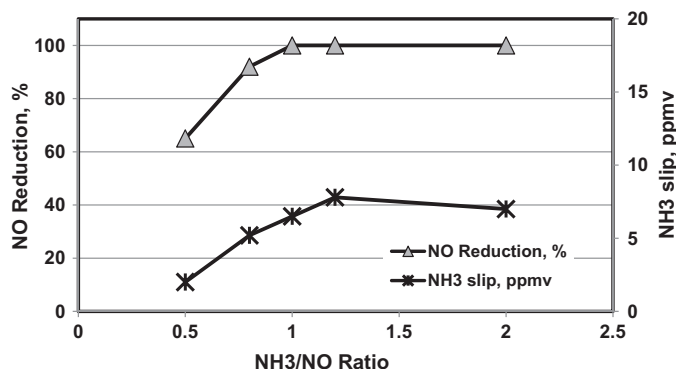**Fig. 8.** Effect of steam on NO conversion (oxidized catalyst).

Fig. 9. Effect of NH_3/NO ratio on NO reduction and NH_3 slip (sulfated catalyst with 10% H_2O).
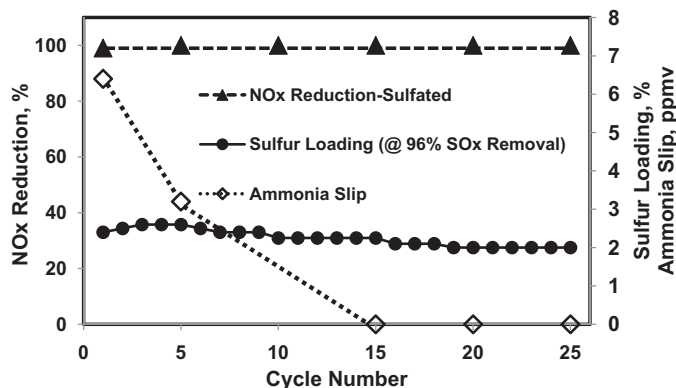

Fig. 10. Sorbent/catalyst performance in cyclic process (with 10% H_2O).

similar trend has also been reported earlier by Jeong et al. [30] and Yeh et al. [32].

3.6. Sorbent/catalyst durability

The long term catalytic activity of the sorbent/catalyst was also determined in a 25-cycle sulfation/regeneration test in a fluidized bed reactor. In each cycle, the sorbent bed (10 cm^3) was sulfated at 450 °C using a simulated flue gas containing 2500 ppmv SO_2, 3.7% O_2, 10% H_2O (balance N_2) at a flow rate at a space velocity of 4000 hr^{-1} until the breakthrough SO_2 in the reactor exit reached 100 ppmv (96% SO_2 removal). The sorbent regeneration tests were carried out with pure methane at 450 °C and 4000 hr^{-1} until the SO_2 exit concentration was below 1 ppmv. The NOx reduction tests were carried out at 450 °C and 4000 hr^{-1} after every five cycles following the sulfation stage by replacing SO_2 with 500 ppmv NO and 500 ppmv NH_3 for about 1 hr, followed by sorbent regeneration. A more detailed description of the experimental procedures can be found in earlier publications [13,35,36]. The results are presented in Fig. 10 indicating that while over 80% of the sulfur capacity of the sorbent/catalyst is maintained and stabilized after 25 sulfation regeneration cycles, the catalytic activity of the sorbent/catalyst for NOx reduction is not affected by the cyclic process. The results also indicate that the ammonia slip gradually decrease in the cyclic process.

4. Conclusion

Simultaneous removal of SO_2 and NOx from flue gases can be accomplished at elevated temperature using a regenerative fluid-bed process based on the utilization of dry regenerable copper-based sorbents. However, highly reactive and attrition resistant sorbents are needed to make these processes economically more attractive than a combined traditional flue gas desulfurization (FGD) and SCR processes.

The results obtained in this study indicate that a highly reactive and attrition resistant regenerable CuO/γ-Al$_2$O$_3$ desulfurization sorbent prepared by a modified sol–gel technique also has a very high catalytic activity for NO$_X$ reduction in SCR reactions and is capable of simultaneously removing close to 100% of both SOx and NOx from a simulated flue gas in a fluidized-bed reactor at NH_3/NOx ratios at or above 1:1. The optimum temperature for NOx reduction in the presence of steam is 350–450 °C, which is similar to the ideal temperature range for the regenerative desulfurization reaction.

The results of the long-term durability tests conducted with the sorbent/catalyst in a fluidized bed indicate a small decrease in its sulfur capacity over the initial 15 cycles, which appeared to stabilize after about 15–25 cycles, while the high catalytic activity of the sorbent is not affected by the cyclic operation. The ammonia slip was determined to be about 6 ppmv with fresh sorbent/catalyst, which gradually decreased to zero after the 15th cycle. The combination of low attrition index coupled with high desulfurization reactivity, excellent regenerability, and high SCR activity indicates that this type of sorbent will be ideal for utilization in a regenerable fluidized bed process for simultaneous removal of SOx/NOx from flue gas at elevated temperatures.

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